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The Influence of Adsorption on *PVT* Measurements in the Gaseous Phase[1]

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PVT measurements of 1,1,1,2-tetrafluoroethane ($C_2H_2F_4$, HFC-134a) and its blend with octofluoropropane (C_3F_8, FC-218) have been performed in the gas phase near the dew curve. The experimental data were obtained by variable-volume and vibrating tube methods. Discrepancies in the behavior of isotherms from their classical behavior were experimentally observed. It was found that the phase transition does not go to completion at a single point of the thermodynamic surface but extends over a limited range of conditions. Obtained results are in accordance with a concept of adsorption of the vapor sample on the surface of the experimental cell. An increase in adsorption under the conditions close to condensation is caused by capillary condensation of the sample at the walls of the cell that initiates an early phase transition. The ranges of diffuse phase transitions were determined for 1,1,1,2-tetrafluoroethane as well as for its mixture with octofluoropropane at different thermodynamic parameters. The influence of selective adsorption on the change in the conditions of phase transition of the 1,1,1,2-tetrafluoroethane/octofluoropropane mixture was also experimentally studied.

KEY WORDS: adsorption; capillary condensation; HFC-134a; HFC-134a/FC-218 mixture; phase transition; *PVT* measurements.

1. INTRODUCTION

Basic *PVT* methods such as constant-volume and variable-volume methods, the vibrating tube method, and others provide high-accuracy experimental

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data[6] over a relatively wide range of thermodynamic parameters. However, due to some methodological uncertainties in the parameters near phase transitions, even careful measurements lead to discrepancies in the behavior of experimental isolines from their classical behavior. Results of the present and other experimental studies reveal the diffuse character of the transition parameters that cannot be attributed to the finite size of the cell or fluctuation phenomena [1]. Recent thermodynamic generalizations of phase transitions [1, 2] are based on the use of the additional function $L(x)$, which defines the relative amount of the sample transferred to the new phase at the single-phase volumetric conditions. According to this method, the thermodynamic potential of the system in the region of the phase transition can be expressed by the following equation:

$$Y(x) = Y^{(\alpha)}(x) + \Delta Y(x)\, L(x) \tag{1}$$

where $\Delta Y(x)$ is the effective change in the thermodynamic function $Y(x)$ and is a thermodynamic potential of the phase α.

In the case of a diffuse phase transition, the function $L(x)$ can be written

$$L(x) = \begin{cases} 0, & x < x_1 \\ L_{1,2}(x), & x_1 < x < x_2 \\ 1, & x > x_2 \end{cases} \tag{2}$$

where x_1 and x_2 are parameters at the beginning and the end of the phase transition. Classical phase transition behavior assumes $L_{1,2}(x) = 0$ and equality of arguments x_1 and x_2.

Nonthermodynamic methods of determining the function $L_{1,2}(x)$ are considered in Ref. 1. However, $L_{1,2}(x)$ is related to the whole thermodynamic system (sample and experimental cell) and, therefore, varies for different experimental conditions. As shown in the present study, the influence of experimental conditions on the change in the parameters of phase transitions may be significant. The paper presents the results of *PVT* measurements of 1,1,1,2-tetrafluoroethane and its blend with octofluoropropane near the dew curve under different thermodynamic conditions. Temperature and concentration changes of phase transition ranges were experimentally observed and were accounted for by the surface effects, namely, by the physical adsorption of the sample and its capillary condensation on the inner surface of the experimental cell.

[6] For most *PVT* methods, the ranges of experimental uncertainties are within 0.005 to 0.05 K, 0.05 to 0.3%, and 0.1 to 0.5% for the temperature, pressure, and density measurements, respectively.

2. DIFFUSE PHASE TRANSITIONS FOR PURE COMPOUND

Two methods, the variable-volume [3] and vibrating tube [4] methods, were applied for the experimental study of *PVT* properties of 1,1,1,2-tetrafluoroethane in the vapor phase near the saturation. An example a of typical experimental isotherm of 1,1,1,2-tetrafluoroethane is given in Fig. 1. Runs were conducted along isotherms starting from point 1. The

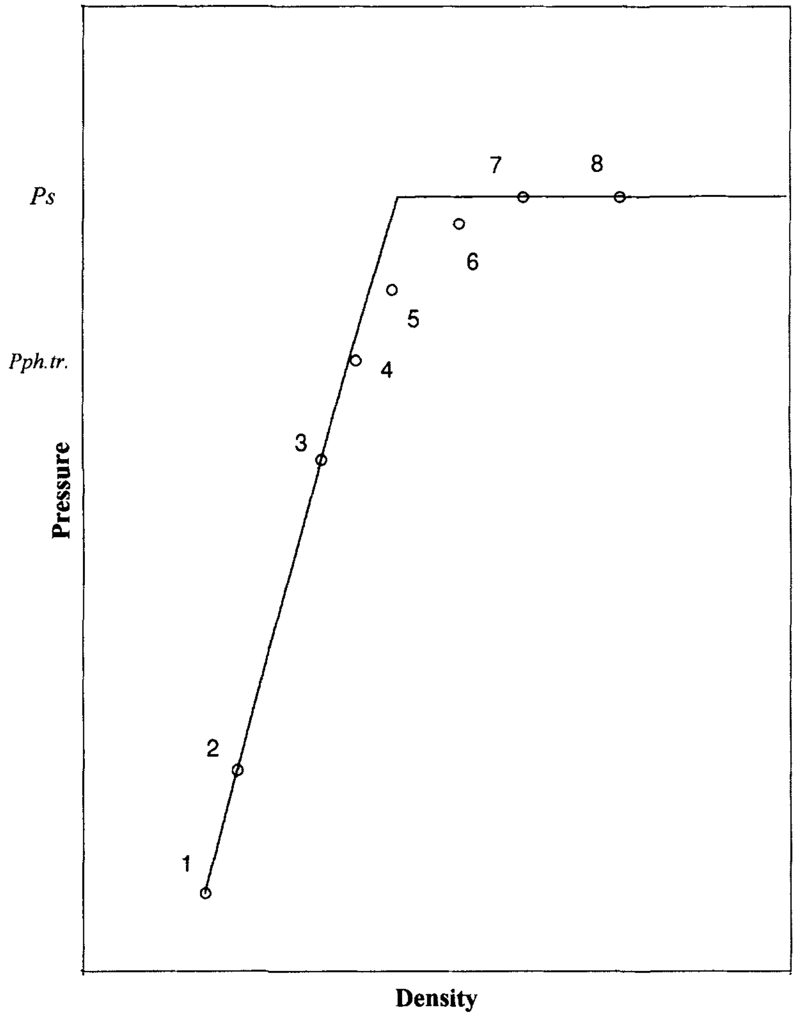

Fig. 1. Typical experimental isotherm in the phase transition range: 1–8 are experimental points.

Table I. Deviations of Vapor Pressures $P_{\text{ph.tr.}}$, at the Beginning of the Phase Transition, from the Vapor Pressures P_s for 1,1,1,2-Tetrafluoroethane

Vibrating tube method		Variable-volume method	
T (K)	δP (%)	T (K)	δP (%)
273.15	−3.33	309.76	−1.55
303.15	−2.20	321.54	−1.16
333.15	−1.79	334.70	−0.80

$\delta P = 100(P_{\text{ph.tr.}} - P_s)/P_s$.

beginning of the phase transition was registered at point 4. It was characterized by a spontaneously increasing pressure and density of the sample, and it was difficult to maintain thermodynamic equilibrium. A phase transition was accompanied by visually observed condensation of the vapor phase at point 5 (variable-volume cell). The curvature of the experimental isotherms in the vapor phase increased monotonically as the dew curve was approached. It did not go to completion at the dew point but extended over a range from point 4 to point 7. Classic behavior of the isotherm was observed later, over the range between point 7 and point 8. Obtained results are characterized by reduction of diffuse phase transitions with increasing temperature for both experimental methods. Deviations of vapor pressures $P_{\text{ph.tr.}}$, at the beginning of the phase transition, from vapor pressures P_s for 1,1,1,2-tetrafluoroethane are given in Table I.

The observed characteristic feature of the behavior of the experimental isotherms is a result of different factors such as impurities in the sample, effect of external fields, and physical adsorption of the substance on the surface surrounding it. Adsorption plays the key role for the vapor–liquid phase transition. A new phase originate in the experimental cell under the conditions corresponding to the vapor phase, i.e., a diffuse phase transition is observed as a result of capillary condensation from the microroughness of the wall surfaces. Capillary condensation occurs at vapor pressures below the saturation pressure, starting at the conditions when the microcapillaries of the cell are covered by a layer of adsorbed molecules [1]. The presence of the liquid phase condensed into the micropores cannot be observed at this stage, but it can be detected by measuring the pressure (point 4). The quantitative difference between the results obtained by the variable-volume and those obtained by the vibrating tube methods may be accounted for by the difference of the materials of the experimental cell and techniques used for approaching the condensation line. The variable-volume cell was made of molybdenum glass, with less microroughness on the inner surface than the stainless-steel vibrating tube. Therefore, the variable-volume cell has a smaller effect on the phase transition. The influence of employed experimental techniques on the change of transition conditions is also different. The pressure was applied to the vapor sample through the pressure-transfer medium (mercury) in a variable-volume method. In the second method, the pressure was increased by introducing an additional amount of the sample into the vibrating tube. Thus, approaching saturation in both experimental methods included mechanical disturbance of the sample that affected the results of the measurements.

3. DIFFUSE PHASE TRANSITIONS FOR THE BINARY MIXTURE

PVT properties near phase transitions were studied for the mixture of 1,1,1,2-tetrafluoroethane and octofluoropropane by a variable-volume method. The experimental results on this system are summarized in Tables II and III. One of the studied isotherms is presented in Fig. 2 for convenience in analysis of obtained results. One can see that the ranges of phase transitions are different depending on the concentration of the mixture. Such differences may be explained by the selective character of adsorption of the components on the surface of the experimental cell. Because physical adsorption increases asymptotically at saturation [5], the adsorption of the component having the lower vapor pressure is predominant. It causes earlier capillary condensation of one of the components accompanied by concentration changes of the volumetric vapor phase. In our measurements, the composition of the investigated mixture changed near saturation because of selective adsorption of 1,1,1,2-tetrafluoroethane. The difference

Table II. Deviations of Vapor Pressures $P''_{\mathrm{ph.tr.}}$, at the Beginning of the Phase Transition, from Dew-Point Pressures P'' for the 1,1,1,2-Tetrafluoroethane/Octofluoropropane Mixture

	$\delta P = 100(P''_{\mathrm{ph.tr.}} - P'')/P''$ (%)				
T (K)	$x^a = 0.266$	$x = 0.358$	$x = 0.419$	$x = 0.751$	$x = 1.0$
285.73	−1.69	−0.92	−2.26	−8.42	
309.76	−1.15	−0.53	−1.50	—	−1.55
320.77	−0.94	−0.45	−1.19	−5.78	—
321.54	—	—	—	—	−1.16
331.78	−0.22	−0.34	—	−3.98	—
334.70	—	—	—	—	−0.80

[a] Mole fraction of 1,1,1,2-tetrafluoroethane.

Table III. *PVT* Properties of the 1,1,1,2-Tetrafluoroethane/Octofluoropropane Mixture in the Region of Phase Transitions (x = Mole Fraction of HFC-134a)

x	T (K)	P (MPa)	ρ (kg · m^{-3})	x	T (K)	P (MPa)	ρ (kg · m^{-3})
0.266	285.73	0.6740	56.69	0.266	331.78	2.2270	236.60
0.266	285.73	0.6798	57.17	0.266	331.78	2.2348	239.14
0.266	285.73	0.6836	57.53	0.266	331.78	2.2426	241.74
0.266	285.73	0.6874	57.91	0.266	331.78	2.2509	244.33
0.266	285.73	0.6912	58.30	0.266	331.78	2.2548	245.68
0.266	285.73	0.6976	58.89	0.266	331.78	2.2587	247.12
0.266	285.73	0.7016	59.39	0.266	331.78	2.2643^b	264.68^b
0.266	285.73	0.7051	61.04	0.266	331.78	2.2662	274.77
0.266	285.73	0.7103^b	71.30^b	0.266	331.78	2.2679	288.53
0.266	285.73	0.7138	98.78	0.266	331.78	2.2688	295.46
0.266	285.73	0.7153	127.73	0.266	331.78	2.2851^a	- -
0.266	285.73	0.7165	185.91	0.358	285.73	0.6960	55.92
0.266	285.73	0.7176	277.10	0.358	285.73	0.6998	56.28
0.266	285.73	0.7175^a	1349.1^a	0.358	285.73	0.7035	56.66
0.266	309.76	1.2923	114.13	0.358	285.73	0.7072	57.04
0.266	309.76	1.3034	115.78	0.358	285.73	0.7110	57.43
0.266	309.76	1.3136	117.16	0.358	285.73	0.7148	57.86
0.266	309.76	1.3231	118.50	0.358	285.73	0.7182	59.24
0.266	309.76	1.3309	119.62	0.358	285.73	0.7204^b	64.96^b
0.266	309.76	1.3367	120.49	0.358	285.73	0.7225	95.50
0.266	309.76	1.3426	121.38	0.358	285.73	0.7232	162.40
0.266	309.76	1.3480	127.55	0.358	285.73	0.7221	260.63
0.266	309.76	1.3515^b	141.44^b	0.358	285.73	0.7218	312.47
0.266	309.76	1.3538	154.96	0.358	285.73	0.7248^a	1344.6^a
0.266	309.76	1.3560	172.04	0.358	309.76	1.3635	117.11
0.266	309.76	1.3582	195.49	0.358	309.76	1.3658	117.37
0.266	309.76	1.3611	280.72	0.358	309.76	1.3674	117.68
0.266	309.76	1.3656	319.47	0.358	309.76	1.3693	117.94
0.266	3.09.76	1.3674^a	1201.9^a	0.358	309.76	1.3703	118.12
0.266	320.77	1.7208	162.75	0.358	309.76	1.3712	118.62
0.266	320.77	1.7267	164.05	0.358	309.76	1.3721	119.43
0.266	320.77	1.7325	164.99	0.358	309.76	1.3732^b	124.32^b
0.266	320.77	1.7364	165.67	0.358	309.76	1.3733	124.68
0.266	320.77	1.7403	166.36	0.358	309.76	1.3747	131.75
0.266	320.77	1.7442	167.01	0.358	309.76	1.3748	130.58
0.266	320.77	1.7501	168.10	0.358	309.76	1.3769	157.95
0.266	320.77	1.7559	171.00	0.358	309.76	1.3788	214.66
0.266	320.77	1.7633^b	201.06^b	0.358	309.76	1.3784	293.65
0.266	320.77	1.7664	211.40	0.358	309.76	1.3807^a	1199.0^a
0.266	320.77	1.7717	271.36	0.358	320.77	1.7778	161.38
0.266	320.77	1.7724	293.22	0.358	320.77	1.7797	162.09
0.266	320.77	1.7809^a	1120.9^a	0.358	320.77	1.7816	162.81

Table III. *(Continued)*

x	T (K)	P (MPa)	ρ (kg · m^{-3})
0.358	320.77	1.7836	163.43
0.358	320.77	1.7855	164.03
0.358	320.77	1.7865	164.51
0.358	320.77	1.7874	165.21
0.358	320.77	1.7884	166.15
0.358	320.77	1.7894[b]	169.13[b]
0.358	320.77	1.7903	171.86
0.358	320.77	1.7914	175.38
0.358	320.77	1.7939	190.33
0.358	320.77	1.7960	222.58
0.358	320.77	1.7974	251.47
0.358	320.77	1.7985	313.63
0.358	320.77	1.8006[a]	1112.1[a]
0.419	285.73	0.5890	48.94
0.419	285.73	0.6380	49.44
0.419	285.73	0.6533	50.38
0.419	285.73	0.6610	51.11
0.419	285.73	0.6687	51.89
0.419	285.73	0.7187[b]	110.88[b]
0.419	285.73	0.7203	148.14
0.419	285.73	0.7230	196.17
0.419	285.73	0.7236	215.36
0.419	285.73	0.7234	228.02
0.419	285.73	0.7235[a]	—
0.419	309.76	1.2779	102.42
0.419	309.76	1.2935	104.24
0.419	309.76	1.3091	106.15
0.419	309.76	1.3325	109.13
0.419	309.76	1.3480	112.04
0.419	309.76	1.3557	115.08
0.419	309.76	1.3576	116.17
0.419	309.76	1.3704[b]	140.94[b]
0.419	309.76	1.3729	156.85
0.419	309.76	1.3769	200.04
0.419	309.76	1.3782	234.59
0.419	309.76	1.3783	249.13
0.419	309.76	1.3783[a]	—
0.419	320.77	1.7146	147.12
0.419	320.77	1.7302	149.68
0.419	320.77	1.7381	150.73
0.419	320.77	1.7458	152.14
0.419	320.77	1.7537	153.32
0.419	320.77	1.7615	154.67
0.419	320.77	1.7692[b]	158.99[b]
0.419	320.77	1.7769	165.79
0.419	320.77	1.7876	194.36
0.419	320.77	1.7940	229.00
0.419	320.77	1.7970	256.01
0.419	320.77	1.7975[a]	—
0.751	285.73	0.5673	37.41
0.751	285.73	0.5691	37.77
0.751	285.73	0.5708	38.16
0.751	285.73	0.5738	39.43
0.751	285.73	0.5964[b]	55.05[b]
0.751	285.73	0.6006	57.81
0.751	285.73	0.6239	89.63
0.751	285.73	0.6376	132.44
0.751	285.73	0.6453	184.44
0.751	285.73	0.6493	220.08
0.751	285.73	0.6572[a]	1286.8[a]
0.751	320.77	1.4718	91.36
0.751	320.77	1.4815	92.30
0.751	320.77	1.4912	93.26
0.751	320.77	1.5009	94.29
0.751	320.77	1.5663[b]	142.39[b]
0.751	320.77	1.5845	175.75
0.751	320.77	1.5992	215.40
0.751	320.77	1.6654[a]	1099.9[a]
0.751	331.78	1.9200	124.61
0.751	331.78	1.9297	125.70
0.751	331.78	1.9395	126.87
0.751	331.78	1.9492	128.06
0.751	331.78	1.9594	129.41
0.751	331.78	1.9692	130.65
0.751	331.78	2.0164[b]	165.30[b]
0.751	331.78	2.0300	184.30
0.751	331.78	2.0432	210.73
0.751	331.78	2.0567	248.77
0.751	331.78	2.0568	252.99
0.751	331.78	2.1103[a]	1027.7[a]

[a] Bubble point.

[b] Condensed phase observed visually.

between P'' (dew-point pressure at initial concentration x) and $P''_{\mathrm{ads.}}$ (pressure at concentration $x_{\mathrm{ads.}}$, which is changed by molecular adsorption) is determined by the slope of the dew-point isotherm on the P–x diagram. The condition $P''_{\mathrm{ads.}} < P''$ ($x = 0.751$) leads to expansion of the parameters of diffuse phase transition, but the condition $P''_{\mathrm{ads.}} > P''$ ($x = 0.266$ and $x = 0.358$) leads to their reduction. The slope of isotherms in the P–x diagram [or derivative $(\partial P''/\partial x)_T$] also determines the magnitude of the change of phase transition conditions. Even small changes in

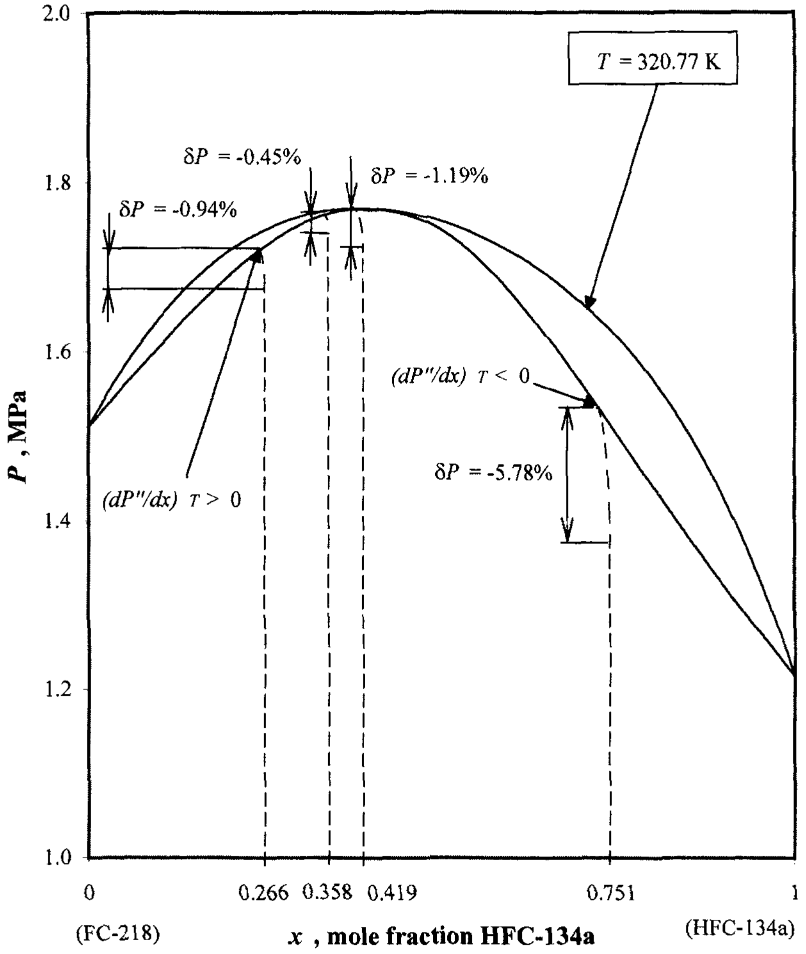

Fig. 2. Phase transition regions at different concentrations of the 1,1,1,2-tetrafluoroethane/octofluoropropane mixture.

the volume concentration of the mixture $x = 0.751$ lead to a considerable increase in the difference $(P'' - P''_{ads.})$. The derivative $(\partial P''/\partial x)_T$ at this concentration is not equal to zero, and the influence of selective adsorption on the phase transition is very high. At a concentration of azeotrope $x = 0.419$, the derivative $(\partial P''/\partial x)_T \to 0$. This means that concentration changes caused by selective adsorption have little or no influence on the value of the dew-point pressure $(P'' \approx P''_{ads.})$. Thus, under thermodynamic conditions $(\partial P''/\partial x)_T \approx 0$, the influence of the selective character of molecular adsorption on the change of parameters of transition is insignificant. It can be confirmed by comparing ranges of phase transitions for azeotropic composition of the mixture and pure 1,1,1,2-tetrafluoroethane (Table II).

4. CONCLUSION

The *PVT* behavior of a 1,1,1,2-tetrafluoroethane/octofluoropropane mixture was experimentally studied in the phase transition region. The diffuse character of the phase transition was determined. The results are in accordance with the concept of early capillary condensation caused by adsorption effects on the inner surface of the cell. The experimentally determined reduction of diffuse phase transitions with increasing temperature is a result of decreasing physical adsorption. At constant temperature the character and magnitude of the change of phase transition parameters are determined by selective adsorption and by the value of the derivative $(\partial P''/\partial x)_T$ at any point on the dew curve. The conclusions made are very important for examining methodological aspects of investigating *PVTx* properties in the phase transition regions as well as for analysis of the experimental results with a view to reducing them to uniform thermodynamic conditions.

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